



Activity and stability of BaKCo/CeO₂ catalysts for diesel soot oxidation

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ABSTRACT

The activity and stability of Ba,K,Co/CeO₂ catalyst in the diesel soot oxidation reaction are studied. Different modes of preparation are analyzed, varying both the cobalt precursor and its order of impregnation. In order to study the stability in a diesel exhaust atmosphere, the catalysts were pretreated in streams of CO₂, H₂O, NO and SO₂. The fresh and the treated catalysts were characterized by FTIR and XRD techniques. The catalytic activity was measured by TPO of soot–catalyst mixtures. The tight contact was used to analyze the intrinsic activity. It was found that the activity was higher for the catalysts prepared using Co(NO₃)₂ compared with the catalysts prepared using Co(AcO)₂. This is because in the former, KNO₃ is present on the catalyst, being this compound very active for this reaction. The thermal stability is lower for the catalyst prepared with Co(NO₃)₂. This catalyst displays a higher K lost when treated at high temperature. When K is present as K₂CO₃, as is the case of the catalysts prepared with Co(AcO)₂, the thermal stability is higher since K₂CO₃ is less volatile than KNO₃. All the catalysts are stable in the presence of mixtures of (CO₂ + H₂O + NO + O₂) having a composition similar to a real diesel exhaust. Under these conditions, the K maintains its original chemical state, either carbonate or nitrate, depending on the precursor used in the catalyst preparation. In presence of SO₂, all the catalysts deactivate due to K₂SO₄ formation, which is not active for soot combustion. However, the sensitivity to SO₂ depends on the precursors used to prepare the catalyst. The Ba,K,Co/CeO₂ catalyst prepared impregnating Co(NO₃)₂ on the Ba,K/CeO₂ catalyst has a higher resistance to the deactivation by SO₂, since the following reaction occurs: Ba(NO₃)₂ + K₂SO₄ → BaSO₄ + KNO₃, which implies that active KNO₃ will disappear slower from the catalytic surface, thus maintaining the activity. TPO experiments of the catalyst in loose contact with soot were also carried out. The Ba,K,Co/CeO₂ catalyst prepared impregnating Co(NO₃)₂ on the Ba,K/CeO₂ catalyst showed the higher activity in loose contact mode.

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1. Introduction

Soot particles and NO_x are the main pollutants emitted from diesel engines. A good alternative to abate these contaminants is the use of catalytic filters in which the soot particles are burnt, and NO_x traps adsorb the NO_x during normal operation and released them as N₂ during the reduction cycles [1]. Potassium improves the contact efficiency between the soot and the catalyst due to the low melting point of K-containing compounds [2,3]. Alkaline metal oxides accelerate the formation of superoxides and peroxides on the surface of cerium oxide, and these species may initiate the soot oxidation [4,5] via the formation of atomic oxygen species (O_{ad}). The adsorption and dissociation of gaseous oxygen on the catalyst surface, are indispensable steps for the combustion to proceed. These surface oxygen species, activated on the catalyst surface are the main oxidizing agents, and their mobility appears to be essential

for an effective catalysis [6]. The mobility of active oxygen species formed on the alkaline metal oxide favors the soot combustion activity by a good catalyst/soot contact [7–10]. We have previously studied the Ba,K/CeO₂ catalysts for this application [11]. Barium plays the role of NO_x adsorbent, and K and CeO₂ are a good combination to oxidize the soot particles. The experiments carried out with Ba,K(x%)/CeO₂ catalysts indicated that the most active catalyst was the one that contained 7 wt% of K [11]. These results suggest that there is a Ce:K ratio for which the synergism is maximum, leading to the most active catalyst. It has been reasonably established that K improves the catalytic activity due to its high mobility, favoring the contact with soot and increasing the surface mobility of oxygen species formed on the K compounds. Therefore, at low K loadings, this component is the one that limits the overall reaction rate. On the other hand, at high K loadings the catalyst surface is fully covered by this compound, and under this condition not enough CeO_x is exposed to the gas phase. This oxide provides the oxygen needed for the oxidation of soot, and then is reoxidized by the oxygen present in the gas phase, due to its well-known redox properties [12]. Therefore, from a mechanistic point of view, at high

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K loadings the reaction rate is controlled by the reoxidation step. The addition of Co improved the behavior of the catalyst as NO_x trap, since the nitro-compounds formed upon treatment with NO_x resulted to be less stable as compared to barium nitrate formed on BaK/CeO₂ catalyst [13–15]. It was found that when cobalt nitrate was added to the Ba,K/CeO₂ catalyst, a high NO_x adsorption capacity was obtained and, what is even more interesting, that the decomposition of the nitrated species occurred at a temperature lower than in the BaK/CeO₂ catalyst. The identification by XRD of a perovskite BaCoO₃ formed upon this preparation procedure was considered to be responsible for the different behavior observed in this particular catalyst [15].

In this work, the activity and stability of Ba,K,Co/CeO₂ catalysts are studied, including the thermal stability and the stability in presence of CO₂, H₂O, NO + O₂ and SO₂, all these compounds being present in the diesel exhaust atmosphere. The influence of Co precursors and the order of impregnations used to prepare the catalyst, on soot combustion activity and stability are also analyzed.

2. Experimental

2.1. Soot and catalyst preparation

The soot used in this work was prepared by burning commercial diesel fuel (Repsol YPF, Argentina) in a glass vessel. After being collected from the vessel walls, it was dried in a stove for 24 h at 120 °C. Its specific surface area was 55 m² g⁻¹. Temperature-programmed experiments performed in a fixed bed reactor, in a TPO-TPD unit, using helium as carrier gas, provided information regarding the amount of partially oxidized groups of the soot surface and the amount of hydrocarbons that could remain adsorbed after the diesel combustion. In this way, it was determined that the amount of carbon released as CO, CO₂, and hydrocarbons represents 9.3% of the soot [16]. The same batch of soot was used in all the experiments presented in this study, to avoid possible differences in surface oxygen groups, which could affect activity results. Samples of soot obtained from a diesel engine were also used, in order to compare the catalytic activity with both types of soot. This sample was provided by the Automobile Gas Emissions Control National Laboratory, and was obtained during an emission test of a light duty engine.

The Ba,K/CeO₂ catalyst was prepared by the wet-impregnation method, using CeO₂ (Sigma, p.a.) as support, to which solutions of Ba(AcO)₂ and KNO₃ were added to obtain loads of 22 wt% of Ba and 7 wt% of K. These values are referred to the CeO₂ support (e.g., 22 g of Ba per 100 g CeO₂). The initial concentration of the starting solutions was 0.1 M of both Ba(AcO)₂ and KNO₃. The suspension was evaporated in a beaker at 100 °C, while being vigorously stirred with a magnetic stirrer until achieving a paste. This paste was dried in a stove for 24 h at 120 °C and calcined for 2 h at 400 °C (fresh catalyst), heating from room temperature to the final temperature in 2 h. The Ba,K,Co/CeO₂ catalysts were prepared by wet-impregnation of the Co precursor on the Ba,K/CeO₂ catalysts calcined at 400 °C (successive impregnations) and also coimpregnating the precursors of barium, potassium and cobalt on the CeO₂ support, in order to obtain a load of 12 wt% of Co. Aqueous solutions of Co(AcO)₂ and Co(NO₃)₂ were used as precursors of cobalt. The Ba,K,Co/CeO₂ catalysts were also calcined at 400 °C. The catalysts prepared by successive impregnations are denoted as (SI), and those prepared by coimpregnation of the three precursors are denoted as (CO). When using Co(NO₃)₂ the catalysts are denoted as Ba,K,Co_N/CeO₂ and when using Co(AcO)₂ the catalysts are denoted as Ba,K,Co_A/CeO₂.

The high load of Ba, which is 20 times higher than the corresponding to the monolayer, has sense since it has been proven that

NO_x not only is absorbed but also is adsorbed on the catalyst [13]. A high Ba load implies a lower reduction cycle time, so a low amount of soot particles is released during the reduction cycle. The 7% of K is the optimum load for a higher soot combustion activity [11]. Finally, the 12% of Co is a very similar molar load as Ba. The Co interaction with Ba generates a more suitable NO_x trap than Ba alone, as explained in a different work [15].

2.2. Catalyst pretreatments

All the pretreatments were carried out in a fixed bed reactor. The thermal stability of the catalysts was evaluated by treating them sequentially at 400 °C, 700 °C, 800 °C and 850 °C during 2 h in air.

The pretreatments with different gases were carried out at 320 °C and at 400 °C during 2 h, loading 0.5 g of sample, and using a flow rate of 60 mL min⁻¹ of gas and afterward purging with air for 1 h at the treatment temperature. In each case the catalyst was heated in air up to the treatment temperature, and afterwards, the air was switched to the treatment gas stream. The mixtures containing CO₂, or NO, were prepared starting from the pure gases and diluting them with air in order to obtain the desired concentration. The gaseous streams for the different pretreatments were:

- Treatment with CO₂: 10% CO₂ in air.
- Treatment with NO + O₂: 1000 ppm NO in air.
- Treatment with H₂O: the air used for the treatment was bubbled in water at 50 °C, in order to obtain a concentration of 12% of water in the air stream at the entrance of the pretreatment cell (fixed bed reactor).
- Treatment with CO₂ + H₂O + NO + O₂: a stream with 10% of CO₂ in air and another stream with 1000 ppm of NO in air were combined, and the resulting stream was bubbled in water at 50 °C, in order to obtain a concentration of 12% of water in the stream at the entrance of the pretreatment cell (fixed bed reactor).

In all cases, the concentration in the gas phase is expressed in a molar basis.

In order to study the stability in an atmosphere containing SO₂, two mixtures of gases were used: a commercial one with 100 ppm of SO₂, and the other one prepared in the laboratory containing 1000 ppm of SO₂, in both cases, diluted with air. The latter, was used to study the stability in an accelerated deactivation test. Therefore, two treatments, both at 400 °C, were adopted to analyze the catalyst stability in SO₂: (i) 1000 ppm of SO₂ for 30 h at 75 mL min⁻¹; (ii) 100 ppm of SO₂ for 40 h at 50 mL min⁻¹. After finishing both treatments, the catalysts were treated in dry air for 2 h at 400 °C.

2.3. Temperature programmed reduction (TPR)–oxidation cycles

Temperature programmed reduction (TPR) experiments were performed in order to test the catalyst stability when operating in oxidation-reduction cycles. The catalyst stability is evaluated by comparing the catalytic activity by TPO, and the cobalt oxidation state, before and after a reduction-oxidation cycle. The TPR experiments were carried out in a fixed bed reactor using a stream of 40 mL min⁻¹ of 5 v/v% of H₂ in Ar, heating at 10 °C min⁻¹. A thermal conductivity detector (TCD) was used to detect the hydrogen consumption. Two reduction-oxidation cycles were carried out, using the following conditions in both cycles:

- Reduction: from 30 °C to 500 °C at 10 °C min⁻¹ in H₂, then cooling down in N₂.
- Oxidation: from 100 °C to 400 °C at 10 °C min⁻¹ in O₂, then cooling down in O₂, and finally purging in N₂ for 30 min.

2.4. Activity test

The catalytic activity for soot combustion was determined by temperature-programmed oxidation (TPO) in a quartz fixed bed reactor, 30 cm long and 1/4 in. in diameter, equipped with a PID temperature controller. The soot particles and the catalysts were mechanically mixed in a mortar to achieve a tight contact [17] during 6 min. The soot/catalyst ratio used in this study was 1/20 (wt/wt). In a standard TPO experiment, a gaseous flow of 40 mL min⁻¹, with 5% O₂ in N₂ was used. Alternatively, a stream of 1000 ppm of NO in air was used as carrier gas. The temperature was increased at a rate of 12 °C min⁻¹. In the TPO experiment, a mass of 10 mg of the catalyst-soot mixture was used. All these experimental conditions (contact mode and mixing time, soot–catalyst ratio, mass loaded into the cell, gas flow rate, oxygen concentration, and heating rate) were carefully studied in order to assure that: (i) all the soot particles are in contact with catalyst and (ii) the reaction occurs under a kinetic-controlled regime, without mass and energy transfer limitations [17]. A modified TPO technique [18] was used. In this technique, the gases that come out of the reactor passed through a methanation reactor, where CO and CO₂ were converted into CH₄. Afterward, methane was measured continuously with a flame ionization detector (FID). The methanation reactor contained a nickel catalyst and operated at 400 °C. A 100% conversion of CO and CO₂ to CH₄ was obtained in the methanator, under the experimental conditions used in this work. The mixing procedure (considering contact mode and mixing time) followed in this study was checked to determine its reproducibility. We found that it is possible to reproduce the TPO profile if the mixing time is controlled [17]. The TPO maximum temperature falls in a window of ±10 °C when two mixtures are prepared using the same batch of catalyst and soot. This is a very good result, mainly if the heterogeneity of the system is taken into account.

In order to evaluate the soot oxidation with a different catalyst–soot contact mode, loose contact mixtures [17] were also prepared with selected catalysts, by shaking the catalysts and the soot in a vial for 6 min.

2.5. Catalysts characterization

- Fourier transformed infrared spectroscopy (FTIR). The spectra were obtained at room conditions, using a Shimadzu IRPrestige 21 spectrometer. Samples were prepared in the form of pressed wafers (ca. 1% sample in KBr). All spectra involved the accumulation of 40 scans at a resolution of 8 cm⁻¹.
- X-ray diffraction (XRD). The X-ray diffractograms were obtained with a Shimadzu XD-D1 instrument, with monochromator, using Cu K α radiation at a scan rate of 4° min⁻¹.
- Atomic absorption spectroscopy (A.A.). This technique was used to determine the K content on the catalysts.

3. Results and discussion

3.1. Catalyst characterization

3.1.1. Fresh catalysts

The phases observed by FTIR and XRD spectroscopies in the Ba,K,Co/CeO₂ fresh catalysts are shown in Table 1. The IR characteristic vibrational frequencies used in the identification are summarized in Table 2. Fig. 1 shows the FTIR spectra corresponding to Ba,K,Co_A/CeO₂ (SI) catalyst (curve a) and Ba,K,Co_N/CeO₂ (SI) catalyst (curve c). Fig. 2 shows the XRD patterns obtained with Ba,K,Co_N/CeO₂ (SI) catalyst (curve a) and Ba,K,Co_A/CeO₂ (SI) catalyst (curve d). FTIR analyses show that cobalt is present as Co₃O₄ spinel in all the samples (Table 1 and Fig. 1), indicating that the

Table 1

Phases found by FTIR and XRD for the catalysts Ba,K,Co/CeO₂ and Ba,K,Co/CeO₂ [2,13].

Catalyst	FTIR phases	XRD phases
Ba,K,Co _N /CeO ₂ (SI)	Ba(NO ₃) ₂ , Co ₃ O ₄ , KNO ₃	CeO ₂ , Ba(NO ₃) ₂
Ba,K,Co _N /CeO ₂ (CO)	BaCO ₃ , Co ₃ O ₄ , KNO ₃	CeO ₂ , BaCO ₃
Ba,K,Co _A /CeO ₂ (SI)	BaCO ₃ , Co ₃ O ₄ , K ₂ CO ₃	CeO ₂ , BaCO ₃
Ba,K,Co _A /CeO ₂ (CO)	BaCO ₃ , Co ₃ O ₄ , K ₂ CO ₃	CeO ₂ , BaCO ₃
Ba,K/CeO ₂	BaCO ₃ , KNO ₃	CeO ₂ , BaCO ₃

Table 2

IR characteristic vibrational frequencies [2,13].

Species	IR vibrational frequencies (cm ⁻¹)
BaCO ₃	1437 (s), 1059 (w), 858 (m), 694 (m)
Ba(NO ₃) ₂	1416 (s), 1358 (s), 818 (m), 730 (m)
O–Ba–NO ₂	1405 (s), 1352 (sh)
Free NO ₃ ⁻¹	1380 (s)
KNO ₃	1433 (sh), 1384 (s), 1354 (sh), 1273 (sh), 826 (m)
K ₂ CO ₃	885 (w), 835 (w)
Co ₃ O ₄	664 (s), 569 (s)
BaSO ₄	1470 (m), 1190 (s), 1130 (s), 1080 (s), 980 (w), 860 (w), 640 (m), 610 (s)
K ₂ SO ₄	1120 (s), 980 (w), 620 (s)

(s): strong; (m): medium; (w): weak; (sh): shoulder.

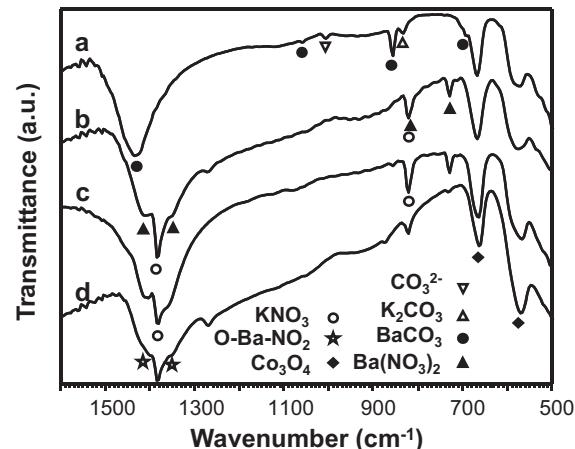


Fig. 1. FTIR spectra for Ba,K,Co_A/CeO₂ (SI) catalyst: (a) fresh, (b) treated with NO + O₂, and for Ba,K,Co_N/CeO₂ (SI) catalyst: (c) fresh, (d) treated with NO + O₂.

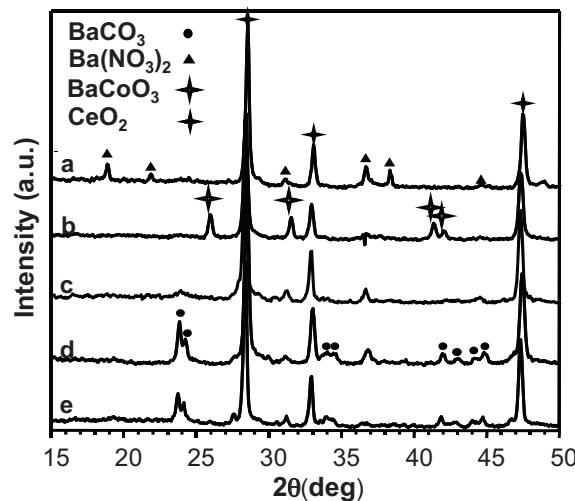


Fig. 2. XRD patterns for Ba,K,Co_N/CeO₂ (SI) catalyst: (a) fresh, (b) treated at 700 °C, (c) treated at 850 °C, and for Ba,K,Co_A/CeO₂ (SI) catalyst: (d) fresh, (e) treated at 850 °C.

final chemical state of this compound does not depend on the precursor used in the preparation. On the other hand, Ba remains as BaCO_3 except in the case of the catalyst prepared by successive impregnation using $\text{Co}(\text{NO}_3)_2$ ($\text{Ba,K,Co}_N/\text{CeO}_2$ (SI)) (compare signals of barium in curves a and c, Fig. 1, and curves d and a, Fig. 2). The $\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) catalyst contains $\text{Ba}(\text{NO}_3)_2$. This suggests that a chemical interaction between Ba, already deposited on the catalyst, and NO_3^- ion from the solution, occurred during the second impregnation. Besides, it can be observed in Fig. 2, curve b, that barium is also forming a mixed oxide with cobalt (BaCoO_3), as it was previously stated [15]. The K chemical state depends on the Co precursor salt used in the preparation. In the case in which the catalyst was prepared using $\text{Co}(\text{NO}_3)_2$, potassium was found mainly as KNO_3 , and when it was prepared with $\text{Co}(\text{AcO})_2$, potassium was found as K_2CO_3 , as indicated in curves c and a in Fig. 1, respectively. The band at 885 cm^{-1} was assigned to K_2CO_3 by comparison with the FTIR spectrum of pure K_2CO_3 (not shown).

Table 1 also shows the data that corresponds to the Ba,K/CeO_2 catalyst. This sample was prepared using KNO_3 and $\text{Ba}(\text{AcO})_2$. The phases present in this catalyst were previously reported [11].

3.1.2. Pre-treated catalysts

The catalysts pre-treated with different gaseous streams underwent significant changes in the Ba and K chemical state. On the other hand, Co_3O_4 was detected in all the catalysts. Table 3 summarizes the phases found in the catalysts pre-treated in different ways.

3.2. Activity of BaKCo/CeO_2 catalysts

3.2.1. Under O_2/N_2 flow

The catalytic activities for soot combustion of Ba,K,Co/CeO_2 catalysts are shown in Fig. 3. The maxima of the TPO profiles (T_M) obtained with the $\text{Ba,K,Co}_N/\text{CeO}_2$ catalysts are approximately 360°C (Fig. 3A, curves a and b), and at 400°C in the case of the $\text{Ba,K,Co}_A/\text{CeO}_2$ catalysts (Fig. 3A, curves c and d). The higher soot combustion activity of the $\text{Ba,K,Co}_N/\text{CeO}_2$ catalysts correlates with the presence of potassium as KNO_3 . Fig. 1 clearly shows the IR bands of K_2CO_3 in the $\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) catalyst (curve a) and the bands of KNO_3 in the $\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) catalysts (curve c). We have previously obtained a similar conclusion [15], when comparing the activity of the fresh $\text{Ba,K,Co}_A/\text{CeO}_2$ catalyst, with that of the catalyst pretreated with high concentrations of $\text{NO} + \text{O}_2$. This treatment led to the transformation of K_2CO_3 into KNO_3 and, consequently, an improvement in the activity for soot combustion was observed. The transformation $\text{K}_2\text{CO}_3 + 2 \text{NO} + 3/2 \text{O}_2 \rightarrow 2 \text{KNO}_3 + \text{CO}_2$ has a favorable ΔG at 300°C , being -42.78 kcal/mol , and at 400°C it is -33.17 kcal/mol . The formation of KNO_3 during the treatment

Table 3

Phases found by FTIR and XRD for the Ba,K,Co/CeO_2 catalysts with different treatments [2,13].

Catalyst	FTIR phases	XRD phases
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated at 850°C	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{K}_2\text{CO}_3$	$\text{CeO}_2, \text{BaCO}_3$
$\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) treated at 700°C	$\text{Co}_3\text{O}_4, \text{KNO}_3$	$\text{CeO}_2, \text{BaCoO}_3$
$\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) treated at 850°C	Co_3O_4	CeO_2
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated in CO_2	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{K}_2\text{CO}_3$	nm ^a
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated in H_2O	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{K}_2\text{CO}_3$	nm
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated in $\text{NO} + \text{O}_2$	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{KNO}_3$	nm
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated in $\text{CO}_2 + \text{H}_2\text{O} + \text{NO} + \text{O}_2$ at 320°C	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{free NO}_3^-$	nm
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated in $\text{CO}_2 + \text{H}_2\text{O} + \text{NO} + \text{O}_2$ at 400°C	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{KNO}_3$	nm
$\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) treated in $\text{CO}_2 + \text{H}_2\text{O} + \text{NO} + \text{O}_2$ at 320°C	$\text{Ba}(\text{NO}_3)_2, \text{Co}_3\text{O}_4, \text{KNO}_3$	nm
$\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) treated in $\text{CO}_2 + \text{H}_2\text{O} + \text{NO} + \text{O}_2$ at 400°C	$\text{Ba}(\text{NO}_3)_2, \text{Co}_3\text{O}_4, \text{KNO}_3$	nm
$\text{Ba,K,Co}_N/\text{CeO}_2$ (SI) treated in SO_2	$\text{Ba}(\text{NO}_3)_2, \text{Co}_3\text{O}_4, \text{KNO}_3, \text{BaSO}_4, \text{K}_2\text{SO}_4$	nm
$\text{Ba,K,Co}_N/\text{CeO}_2$ (CO) treated in SO_2	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{KNO}_3, \text{BaSO}_4, \text{K}_2\text{SO}_4$	nm
$\text{Ba,K,Co}_A/\text{CeO}_2$ (SI) treated in SO_2	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{K}_2\text{CO}_3, \text{BaSO}_4, \text{K}_2\text{SO}_4$	nm
$\text{Ba,K,Co}_A/\text{CeO}_2$ (CO) treated in SO_2	$\text{BaCO}_3, \text{Co}_3\text{O}_4, \text{K}_2\text{CO}_3, \text{BaSO}_4, \text{K}_2\text{SO}_4$	nm

^a Not measured.

with $\text{NO} + \text{O}_2$ is detected by the FTIR analysis, as shown in Fig. 1, curve b, in agreement with the thermodynamics data. The higher activity of the catalysts containing KNO_3 in comparison with the catalysts containing K_2CO_3 can be correlated with the higher mobility of KNO_3 present in the former. It is known that the activity in loose contact correlates with the Tamman temperature of the compounds present in the catalytic surface. This characteristic temperature is approximately half of the melting point, and is related to the mobility of the species on the catalytic surface [19]. The lower the value of the Tamman temperature, the higher the compound mobility on the surface, thus increasing the probability of contact between the catalyst and the soot particles and consequently increasing the catalytic activity. The melting points of KNO_3 and K_2CO_3 are 333°C and 891°C , respectively. Therefore, the higher activity observed with the catalysts that contain KNO_3 correlates with the higher mobility of this compound. Additionally, as mentioned in Section 1, the active oxygen species for soot combustion are formed on the K-containing compounds, and therefore, a higher activity was correlated with a higher mobility of these species [6–10].

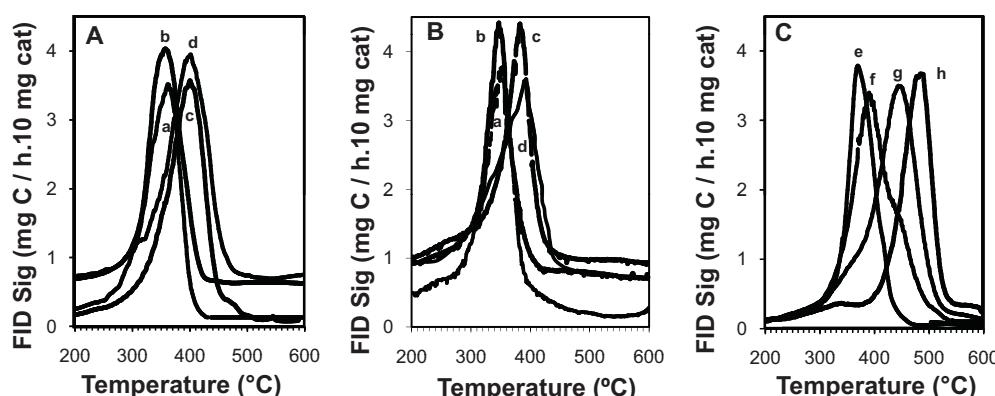


Fig. 3. TPO profiles using O_2/N_2 (A and C) and NO/air (B) of tight contact mixtures of soot and catalyst: (a) $\text{Ba,K,Co}_N/\text{CeO}_2$ (SI), (b) $\text{Ba,K,Co}_N/\text{CeO}_2$ (CO), (c) $\text{Ba,K,Co}_A/\text{CeO}_2$ (SI), (d) $\text{Ba,K,Co}_A/\text{CeO}_2$ (CO), (e) $\text{KNO}_3/\text{CeO}_2$, (f) $\text{K}_2\text{CO}_3/\text{CeO}_2$, (g) Co/CeO_2 , and (h) Ba/CeO_2 .

3.2.2. Under NO/air flow

Fig. 3B shows the TPO profiles obtained using NO/air as carrier gas. For both Ba,K_xCo_N/CeO₂ catalysts (curves a and b), the T_M shifted only 10 °C to lower temperature comparing with the TPO profiles obtained using O₂/N₂ as carrier gas. In the case of the Ba,K,Co_A/CeO₂ catalysts (curves c and d) the T_M shifted 20 °C to lower temperature. As discussed below, when the catalyst is exposed to CO₂, for example during soot combustion, potassium carbonatation takes place in certain extent. In the case that NO is present during this combustion, potassium carbonatation and nitration are competing reactions. The catalyst activity depends upon which of these two reactions is faster. If nitration prevails, the catalyst is kept in the more active way. In the case of the Ba,K,Co_A/CeO₂ catalysts, where potassium is mainly as K₂CO₃, the effect of potassium nitration on activity is more important. Although KNO₃ is formed in all the catalysts regardless the K precursor used in the catalyst preparation, the fresh catalyst containing KNO₃ are initially, more active than the fresh catalyst containing K₂CO₃, even in an atmosphere with NO, as can be observed in Fig. 3A. The Y-axis in this figure is the combustion rate, expressed as (mg C/h 10 mg cat). The slope of each TPO profile represents how fast the reaction rate changes. It can be clearly seen in Fig. 3A that the slopes for the fresh catalysts containing KNO₃ (curves a and b) are more pronounced than the slopes for the fresh catalysts containing K₂CO₃, which is consistent with above discussion, and shows that the transformation of K₂CO₃ to KNO₃ is comparatively low.

On the other hand, there might be a contribution of NO₂ in the soot oxidation for all the catalysts, due to the conversion of NO to NO₂. However, this gas phase contribution to soot combustion is negligible under our experimental conditions, as will be shown in the last section of this work.

The activities of the Ba,K,Co_N/CeO₂ catalysts are the same, regardless the chemical state of barium (Fig. 3A, curves a and b). The addition of barium to K/CeO₂ catalyst does not improve the catalytic activity [11], although the dispersion of the barium compound can be different, and consequently it can affect the effective K-CeO₂ surface ratio. The soot combustion activity depends on this ratio [11]. However, if this ratio is kept within a given range, the changes in activity are negligible. On the other hand, the activities of Ba,K,Co_N/CeO₂ and Ba,K,Co_A/CeO₂ catalysts are different (compare curves a and b with curves c and d in Fig. 3A), even though cobalt is present as Co₃O₄ in all of them. Then, the chemical state of potassium is the determinant factor of the level of activity of Ba,K,Co/CeO₂ catalysts, as can be seen also in Fig. 3C, where the order of soot combustion activity is: KNO₃/CeO₂ > K₂CO₃/CeO₂ and K/CeO₂ > Co/CeO₂ > Ba/CeO₂. Moreover, the presence of Co and Ba on the K/CeO₂ catalyst did not affect its catalytic activity. As mentioned in Section 1, Ba and Co were added into the catalyst due to their properties as NO_x traps. In the Ba,K,Co/CeO₂ catalyst, K and Ce play a relevant role in soot oxidation.

3.3. Behavior as NO_x trap

The redox behavior of NO_x traps is important, since the catalyst shall operate alternately under oxidizing and reducing atmospheres. Therefore, it is important to know if these different atmospheres would affect the catalyst activity for soot combustion. In order to study this issue, the Ba,K,Co_N/CeO₂ (SI) catalyst was treated in two consecutive cycles of reduction (with H₂) and oxidation. Between each treatment in H₂, the catalyst was oxidized in O₂. Afterwards, the catalyst was mixed with soot and its activity for soot combustion was evaluated by TPO. The TPO profile of the treated catalyst was different to that of the fresh catalyst. The T_M for the latter was 360 °C, while for the treated catalyst in TPR-TPO cycles was 400 °C (TPO profiles not shown). The TPR experiments

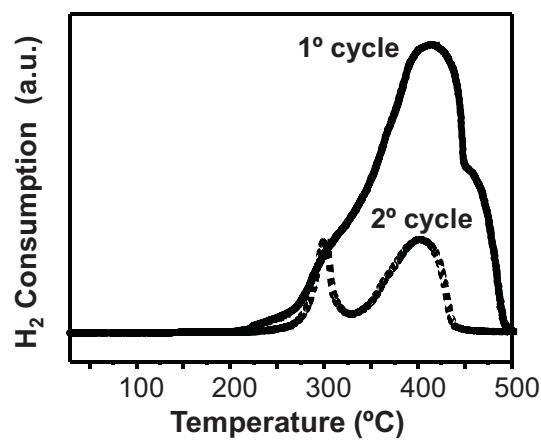


Fig. 4. TPR corresponding to the reduction-oxidation cycles for Ba,K,Co_N/CeO₂ (SI) catalyst.

for both, the first and the second cycle, show the maxima signals at the same temperature ($T_M = 300$ °C and $T_M = 400$ °C for the first and the second maxima, respectively) (Fig. 4), although with different intensities. The first peak in the TPR profile that corresponds to the 2nd cycle coincides with the low temperature shoulder of the main peak displayed in the first TPR cycle. The difference in activity between the fresh and the treated catalyst is due to the KNO₃ reduction, represented by the shoulder at 450 °C in the TPR profile for the first cycle (see Fig. 4). Consequently, the maximum in the TPO profile of the catalyst after being treated in TPR experiments is at 400 °C, the same as in the Ba,K,Co_A/CeO₂ catalysts, in which KNO₃ is not present. Although a K loss due to the treatment at 500 °C may occur to some extent, this is not the main cause for the lower T_M observed in the TPO experiment, as will be shown in the next section. For example it is remarkable that after the treatment of the catalyst at 700 °C during 2 h, the activity was higher ($T_M = 374$ °C, result not shown) than after heating up the same catalyst up to 500 °C during the reduction cycle ($T_M = 381$ °C).

3.4. Thermal stability

In order to study the catalysts thermal stabilities, sequential treatments of 2 h at 400 °C, 700 °C, 800 °C and 850 °C were carried out, analyzing the phases present after each treatment by FTIR and XRD. Table 1 shows the phases found in these catalysts. It was found an excellent thermal stability for the Ba,K,Co_A/CeO₂ (SI) catalyst, as can be observed in the TPO profiles shown in Fig. 5A. In this catalyst, the thermal treatments did not lead to any change in the phases present on it, as observed by XRD and FTIR analyses. The potassium loss was 5% after the treatment at 850 °C, as analyzed by A.A. On the contrary, the Ba,K,Co_N/CeO₂ (SI) catalyst, progressively losses its activity as the severity of the thermal treatment increases (Fig. 5B). Other experiment was carried out, by treating the catalyst at 400 °C during 11 h. The TPO profile displayed a similar T_M value as the fresh catalyst (result not shown). Therefore, it can be concluded that this catalyst losses activity at high temperature (700 °C or higher) and is stable at 400 °C. The bands of KNO₃ decreased after the treatment at 700 °C (compare curves b and a, Fig. 6). At this temperature, the Ba(NO₃)₂ decomposition also occurred, as observed by XRD analyses (compare curves b and a, Fig. 2) and FTIR (compare curves b and a, Fig. 6). On the other hand, the formation of BaCoO₃ perovskite was observed by XRD (curve b, Fig. 2). This perovskite was not observed at 850 °C (curve c, Fig. 2). The potassium content decreased 40% after the treatment at 850 °C, consequently, this loss of potassium is the reason of the catalyst deactivation. The higher thermal stability of Ba,K,Co_A/CeO₂ (SI) catalyst is due to the

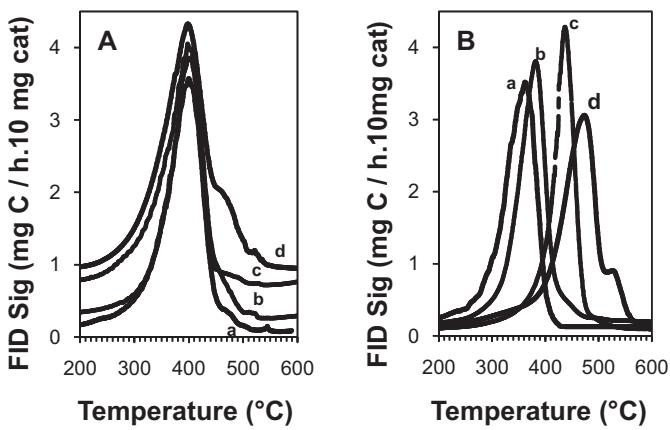


Fig. 5. TPO profiles using O_2/N_2 of tight contact mixtures: (A) Ba,K,Co_A/CeO₂ (SI) catalyst and (B) Ba,K,Co_N/CeO₂ (SI) catalyst. Pretreatments: (a) fresh, (b) 700 °C, (c) 800 °C, and (d) 850 °C.

presence of K as K₂CO₃, which is a more stable compound than KNO₃, which is the chemical state of K when the catalyst is prepared using Co(NO₃)₂.

The activities of Ba,K,Co_N/CeO₂ (CO) catalysts treated at 700 °C ($T_M = 374$ °C) and treated at 800 °C ($T_M = 420$ °C) (results not shown) were slightly higher than those for Ba,K,Co_N/CeO₂ (SI) catalysts with the same treatments ($T_M = 381$ °C and $T_M = 437$ °C, respectively), although both catalysts contain KNO₃. The reason of this is not completely clear. Taking into account that the Ba,K,Co_N/CeO₂ (SI) catalyst contains the BaCoO₃ perovskite, it might be possible that the interaction between KNO₃ with this phase is weaker than the interaction with CeO₂, which is the predominant phase in the Ba,K,Co_N/CeO₂ (CO) catalyst. In Section 1, as well as in Section 3.2, we correlated the higher soot combustion activity with the higher K mobility, which increases the probability of soot–catalyst contact. Then, the lower the K interaction with the catalyst surface, the higher the mobility and the higher the catalyst activity. On the other hand, if the K interaction with the support is too low, a decrease in the thermal stability is observed. Nevertheless, this issue needs a specific research to be fully understood.

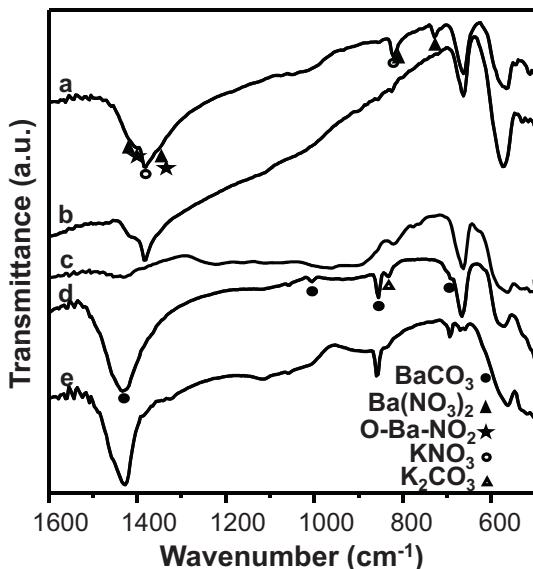


Fig. 6. FTIR spectra for Ba,K,Co_N/CeO₂ (SI) catalyst: (a) fresh, (b) treated at 700 °C, (c) treated at 850 °C, and for Ba,K,Co_A/CeO₂ (SI) catalyst: (d) fresh, (e) treated at 850 °C.

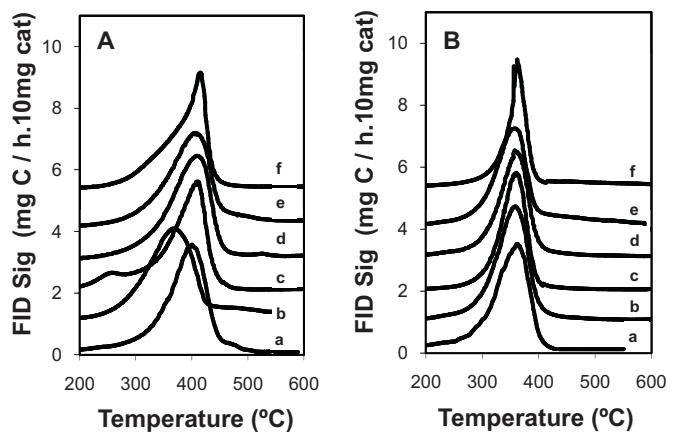


Fig. 7. TPO profiles using O_2/N_2 of tight contact mixtures of soot and catalyst: (A) Ba,K,Co_A/CeO₂ (SI) and (B) Ba,K,Co_N/CeO₂ (SI). (a) Fresh, (b) treated with $NO + O_2$ at 320 °C, (c) H_2O at 320 °C, (d) CO_2 at 320 °C, (e) $CO_2 + H_2O + NO + O_2$ at 320 °C, and (f) $CO_2 + H_2O + NO + O_2$ at 400 °C.

CeO₂ support with its redox property has the role of exchanging oxygen with the gas phase, and then it should remain as such, without forming cerium carbonate, nitrate or hydroxide, in order to keep the redox property. The XRD patterns for Ba,K,Co_A/CeO₂ (SI) and Ba,K,Co_N/CeO₂ (SI) catalysts, fresh and treated, showed that CeO₂ is present in both of them (Tables 1 and 3).

3.5. Stability in the presence of $NO + O_2 + CO_2 + H_2O$

The atmosphere of a diesel exhaust contains $NO + O_2 + CO_2 + H_2O$. Then, in order to evaluate the catalytic stability in this atmosphere, the catalysts were treated with gaseous streams containing alternatively $NO + O_2$, CO_2 , wet air, and all of them, in concentrations within the ranges of a real diesel exhaust, at 320 °C and at 400 °C. Both treatments, at 320 °C and at 400 °C, provoked the same changes in activity and led to the formation of the same phases, as observed by FTIR. Table 3 summarizes the phases found in the catalysts after the different treatments. Figs. 7 and 8 show the TPO profiles and the FTIR spectra, respectively, corresponding both to Ba,K,Co_A/CeO₂ (SI) and Ba,K,Co_N/CeO₂ (SI) catalysts with different treatments. The Ba,K,Co_A/CeO₂ (SI) catalyst treated with CO_2 did not show changes in activity, as can be observed in Fig. 7A, curves a and d, respectively. There was a change in the bands that corresponds to K₂CO₃, as shown in Fig. 8, curves a and b. The band at 880 cm⁻¹ corresponding to bulk carbonate is displayed in the spectrum of the catalyst treated with CO_2 (curve b), while the band at 835 cm⁻¹ displayed in the fresh catalyst spectrum (curve a), corresponding to surface carbonate, decreased its intensity. The treatment with wet air led to similar changes in the IR bands. The hydroxide band (around 3400–3700 cm⁻¹) was not observed in the catalyst treated with wet air, while the band that corresponds to K₂CO₃ appeared after this treatment (Fig. 8, curve c), due to carbonates formed with the CO_2 present in the air used in the treatment. This treatment did not deactivate the catalyst (Fig. 7A, curve c). On the other hand, the treatments in $NO + O_2$ led to catalyst activation (Fig. 7A, curve b) due to KNO₃ formation (observe the bands at 1385 and 825 cm⁻¹ in Fig. 8, curve d). The catalysts treated with $NO + O_2 + CO_2 + H_2O$ at 320 °C and at 400 °C have the same activity as the catalysts treated with CO_2 (Fig. 7A, curves e and f), although competitive adsorption between carbonates and nitrates exists (the free nitrate band at 1385 cm⁻¹ is observed but the KNO₃ band at 825 cm⁻¹ is not, as seen in Fig. 8, curves e and f). The Ba,K,Co_N/CeO₂ (SI) catalyst is stable after being exposed to different atmospheres (Fig. 7B), since no K₂CO₃ is formed from KNO₃, as seen in Fig. 8, curves h and i.

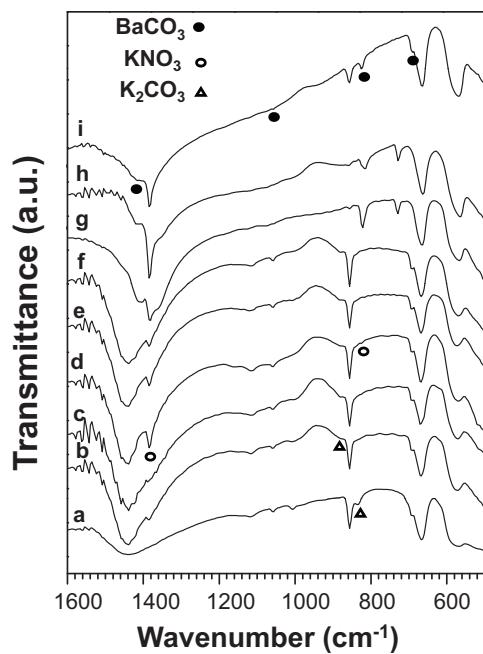


Fig. 8. FTIR spectra for Ba,K,CoA/CeO₂ (SI) catalyst: (a) fresh, (b) treated with CO₂ at 320 °C, (c) H₂O at 320 °C, (d) NO + O₂ at 320 °C, (e) CO₂ + H₂O + NO + O₂ at 320 °C, (f) CO₂ + H₂O + NO + O₂ at 400 °C; for Ba,K,Co_N/CeO₂ (SI) catalyst: (g) fresh, (h) treated with CO₂ + H₂O + NO + O₂ at 320 °C, and (i) CO₂ + H₂O + NO + O₂ at 400 °C.

Only BaCO₃ is formed at 400 °C, but this change does not affect the catalyst activity.

As previously mentioned, CeO₂ should remains as such without forming cerium nitrate, carbonate or hydroxide. It was proven that CeO₂ do not interact with NO + O₂ at NO concentrations higher than the used in this work, between 70 °C and 490 °C [14], and do not interact with CO₂ during experiments of pulses of CO₂, between 25 °C and 500 °C [20]. In addition, hydroxide species were not observed by FTIR (zone of 3000–4000 cm⁻¹, not shown in Fig. 8). Consequently, the CeO₂ maintains its surface composition even after exposure to a gas stream with a composition similar to that of a real exhaust.

3.6. Stability in the presence of SO₂

In order to analyze the stability of Ba,K,Co/CeO₂ catalysts in a SO₂-containing atmosphere, these catalysts were treated at 400 °C with a stream of 50 mL min⁻¹ containing 100 ppm of SO₂, during 40 h. Table 3 summarizes the phases found in the catalysts after this treatment. The Ba,K/CeO₂ catalyst treated in this way formed barium, potassium and cerium sulfates, as observed by FTIR [11]. These sulfates were also observed in the Ba,K,Co/CeO₂ catalysts (Fig. 9 and Table 3). Comparing the TPO profiles of the poisoned Ba,K,Co/CeO₂ catalysts (Fig. 10), it can be observed that three of the four catalysts prepared presented the same value of T_M (curves d, f and h, corresponding to Ba,K,Co_N/CeO₂ (CO), Ba,K,Co_A/CeO₂ (SI) and Ba,K,Co_A/CeO₂ (CO) catalysts, respectively). All of them presented a slight deactivation after the treatment with SO₂ (compare with curves c, e and g, obtained with the fresh catalysts). It is very interesting that the Ba,K,Co_N/CeO₂ (SI) catalyst was not deactivated (compare curves a for the fresh catalyst with curve b for the treated catalyst). The FTIR spectra of these catalysts show that the bands of K₂SO₄ (1120, 980 and 620 cm⁻¹) are more defined in the case of the catalysts that showed deactivation (curves d, f and h), while the bands of BaSO₄ (1190, 1130, 1080, 980 and 640 cm⁻¹) are more defined in the catalyst which did not show deactivation (curve b).

The transformation of barium into BaSO₄ is not relevant for the soot

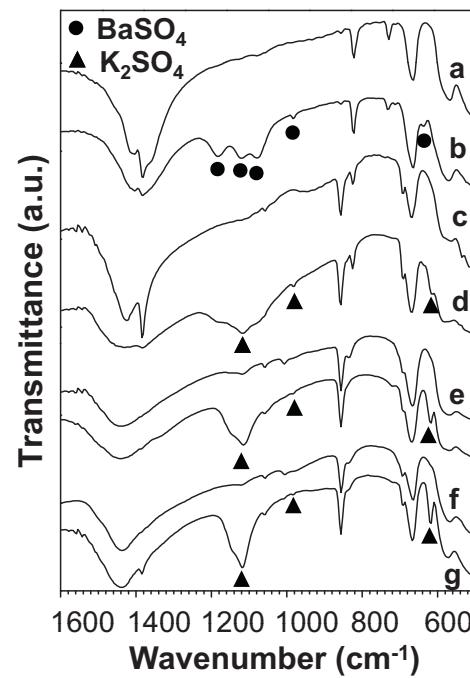


Fig. 9. FTIR spectra for the catalysts Ba,K,Co_N/CeO₂ (SI): (a) fresh, (b) treated with SO₂; for Ba,K,Co_N/CeO₂ (CO): (c) fresh, (d) treated with SO₂; for Ba,K,Co_A/CeO₂ (SI): (e) fresh, (f) treated with SO₂; for Ba,K,Co_A/CeO₂ (CO): (g) fresh, (h) treated with SO₂.

oxidation reaction, as discussed before in Section 3.2 and shown in curve h of Fig. 3C. On the other hand, the K state is critical for soot oxidation. When KNO₃ or K₂CO₃ are converted into K₂SO₄, the catalytic activity decreases. The melting point of the K₂SO₄ is very high (1069 °C), thus decreasing the K mobility and consequently the catalytic activity. These data indicate that the deactivation related to the soot oxidation reaction is due to the loss of an active species of potassium, such as KNO₃ and K₂CO₃, which were transformed in

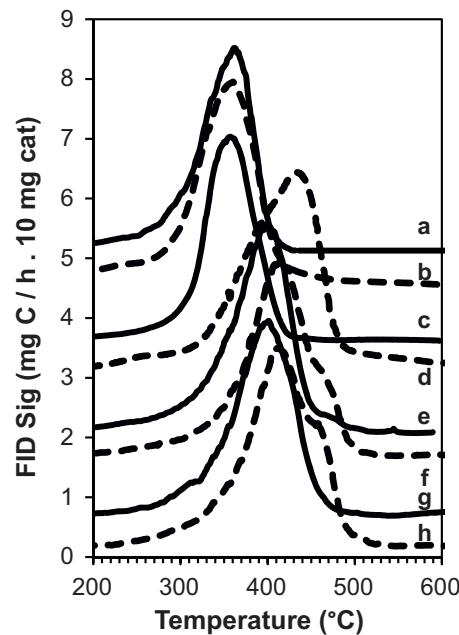


Fig. 10. TPO profiles using O₂/N₂ of tight contact mixtures of soot and catalyst: Ba,K,Co_N/CeO₂ (SI): (a) fresh, (b) treated with SO₂, Ba,K,Co_N/CeO₂ (CO); (c) fresh, (d) treated with SO₂, Ba,K,Co_A/CeO₂ (SI); (e) fresh, (f) treated with SO₂, Ba,K,Co_A/CeO₂ (CO); (g) fresh, (h) treated with SO₂.

another component, inactive for this reaction, such as the K_2SO_4 . The higher $BaSO_4/K_2SO_4$ ratio observed in the catalyst which did not suffer deactivation is due to the following reaction:



This reaction is only possible in the $Ba,K,Co_N/CeO_2$ (SI) catalyst, since this is the only one in which barium is present as $Ba(NO_3)_2$. In the other catalysts, barium is present as $BaCO_3$. Once all the barium is transformed into $BaSO_4$, the KNO_3 would be irreversibly transformed into K_2SO_4 and the catalyst will be deactivated. In fact, a more severe treatment of the $Ba,K,Co_N/CeO_2$ (SI) catalyst with SO_2 (1000 ppm of SO_2 during 30 h at 75 mL min^{-1}) led to catalyst deactivation, since during this treatment all the barium was completely sulfated in a shorter time (results not shown). The reaction (1) was also proposed to explain the stability in the case of $Ba,K/CeO_2$ catalyst [13]. The $BaCO_3$ present in the fresh $Ba,K/CeO_2$ catalyst, is transformed into $Ba(NO_3)_2$ after the treatment with high concentrations of $NO + O_2$. The $Ba,K/CeO_2$ catalyst poisoned with SO_2 , recovered the activity after it was treated with $NO + O_2$. This is due to the formation of $Ba(NO_3)_2$, which then reacts with K_2SO_4 regenerating the active K through reaction (1). The IR bands of K_2SO_4 observed in the deactivated catalyst decreased after the treatment with $NO + O_2$ to the expense of higher $BaSO_4$ formation. In summary, during the treatment with SO_2 , K_2SO_4 is formed in the four catalysts prepared in this work, leading to their deactivation. The reaction $K_2SO_4 + NO + O_2 \rightarrow KNO_3 + SO_2$ has a high positive standard free energy change (45.02 kcal/mol at $490^\circ C$). On the other hand the reaction $Ba(NO_3)_2 + K_2SO_4 \rightarrow BaSO_4 + KNO_3$ has a slightly positive standard free energy change (1.49 kcal/mol at $490^\circ C$). Consequently, even though the equilibrium constant has a rather small value, this latter reaction will show a certain degree of conversion. This reaction can occur only with the $Ba,K,Co_N/CeO_2$ (SI) catalyst, since this is the only one in which barium is present as $Ba(NO_3)_2$. This reaction regenerates active K and, consequently, the catalyst can be active for more time, as long as $Ba(NO_3)_2$ be present in the catalyst.

3.7. Activity in loose contact

The experiments described above were carried out using the tight-contact mode between the soot and the catalyst [17]. This is useful to study intrinsic activities and stabilities, without masking the results with mass and energy transfer limitations. In order to have a different approximation to the real situation, the catalyst and the soot particles were mixed in loose contact [17], as described in Section 2. Fig. 11A shows the TPO profiles obtained with the four $Ba,K,Co/CeO_2$ catalysts prepared in this work. In the $Ba,K,Co_N/CeO_2$ catalysts, the potassium is present as KNO_3 . The TPO obtained with these catalysts prepared either by sequential or co-impregnation are shown in Fig. 11A, curves a and b, respectively. In the case of the $Ba,K,Co_A/CeO_2$ catalysts, the potassium is present as K_2CO_3 , and the TPO that corresponds to these catalysts are shown in curves c and d, Fig. 11A. As mentioned in Section 3.2, the higher mobility of the K compound correlates with the higher activity for soot oxidation. The higher activity observed in loose contact with the catalysts that contain KNO_3 correlates with the higher mobility of this compound. On the other hand, the fact that $Ba,K,Co_N/CeO_2$ (SI) (curve a) catalyst is more active in loose contact than $Ba,K,Co_N/CeO_2$ (CO) (curve b) catalyst, could be explained in terms of the higher mobility of KNO_3 in the former, due to a lower interaction of K with the surface, in agreement with above discussion (the higher the mobility, the higher the activity). This higher activity of the $Ba,K,Co_N/CeO_2$ (SI) catalyst, and its lower thermal stability, can be explained by the lower interaction of K with the surface due to the presence of the perovskite phase. Nevertheless, this issue requires further research. Fig. 11B shows the TPO profiles for $Ba,K,Co_N/CeO_2$ (SI)

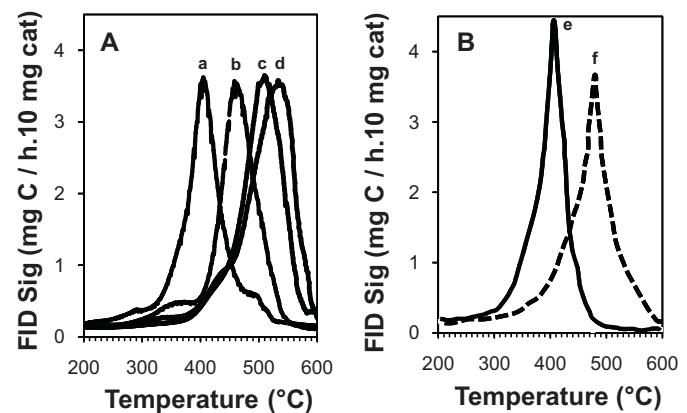


Fig. 11. TPO profiles using: (A) O_2/N_2 and (B) NO/air , of loose contact mixtures of soot and catalyst: $Ba,K,Co_N/CeO_2$ (SI) (a and e), $Ba,K,Co_N/CeO_2$ (CO) (b), $Ba,K,Co_A/CeO_2$ (SI) (c and f) and $Ba,K,Co_A/CeO_2$ (CO) (d).

(curve e) and for $Ba,K,Co_A/CeO_2$ (SI) (curve f) when using NO/air . The increase in activity when using NO/air with $Ba,K,Co_A/CeO_2$ (SI) catalyst as compared to the use of O_2/N_2 (compare curve c with $T_M = 540^\circ C$ and curve f with $T_M = 480^\circ C$) can be attributed to potassium nitration, as was discussed before. Since no activity change was observed in the case of $Ba,K,Co_N/CeO_2$ (SI) when using NO/air (compare curves a and e), it can be concluded that there is no contribution of gas phase NO_2 to soot oxidation under these conditions. It is known that NO_2 is more oxidant than O_2 in gas phase reactions. However, O_2 is not the real oxidant in our catalyst. It has been proposed that the oxidant species for soot oxidation on K/CeO_2 catalyst are the superoxide and peroxide species [21]. The more important observation is that, for $Ba,K,Co_N/CeO_2$ (SI), the difference in T_M between tight and loose contact is only 40 °C. This means that in a real situation, this difference could be even lower since the type of contact that we used in the so-called “loose contact mode”, is really very poor. It can be expected that the contact between the soot particles and the catalyst deposited on a real filter could be better than this type of contact. This difference in T_M is very low, which is very good considering the results reported in the literature [8,22–26].

3.8. Validation of our experiments using a homemade soot by comparison with a real soot

Fig. 12 shows the TPO experiments for the combustion of soot with fresh $Ba,K,Co_N/CeO_2$ (SI) catalyst (A) and fresh $Ba,K,Co_A/CeO_2$ (SI) catalyst (B). Curves a represent the experiments with

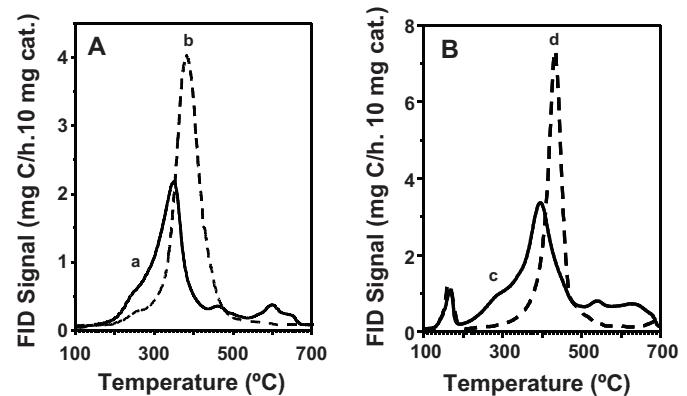


Fig. 12. TPO profiles using: (A) $Ba,K,Co_N/CeO_2$ (SI) and (B) $Ba,K,Co_A/CeO_2$ (SI), of tight contact mixtures of catalyst with homemade soot (a) or real soot (b).

homemade soot and curves b with real soot. The onset temperature of real soot is lower than the corresponding to homemade soot in both catalysts. Also the T_M is lower, indicating that real soot is more reactive than our homemade soot. These results indicate that our homemade soot is useful to evaluate the reactivity of real soot. Atriback et al. [27] also found that his model soot samples are less reactive than real soot samples, which can be attributed, mainly, to a lower proportion of oxygen and other heteroatoms, and also to a negligible ash content and very high fixed carbon content. In the same trend, Nejar et al. [28] observed that hydrogen and oxygen content are related to the presence of surface complexes that increase the carbon reactivity. They also stated that the ashes are able to catalyse the carbon oxidation reaction affecting also the carbon reactivity.

4. Conclusions

In this work, the activity of Ba,K,Co_N/CeO₂ catalysts and their stabilities in conditions of a diesel exhaust atmosphere were studied. The higher activity of catalysts prepared using cobalt nitrate as precursor (Ba,K,Co_N/CeO₂) was correlated with the presence of potassium as KNO₃. The activity for soot oxidation in loose contact for Ba,K,Co_N/CeO₂ (SI) was not very different from that in tight contact mode, being the difference in T_M only 40 °C.

The Ba,K,Co_N/CeO₂ catalyst deactivates when treated at high temperatures (800 °C or higher temperatures) due to the loss of potassium by volatilization. The thermal stability was higher for Ba,K,Co_A/CeO₂ catalyst since K₂CO₃ present on this catalyst is less volatile than KNO₃, which is present on Ba,K,Co_N/CeO₂ catalysts.

The Ba,K,Co_A/CeO₂ (SI) catalyst keeps its activity when exposed to an atmosphere containing NO + O₂ + CO₂ + H₂O since K₂CO₃ predominates over KNO₃ on the catalytic surface.

All Ba,K,Co/CeO₂ catalysts are poisoned with SO₂ at 400 °C. However, the Ba,K,Co_N/CeO₂ (SI) catalyst has a higher resistance to the deactivation by SO₂, since the following reaction occurs: Ba(NO₃)₂ + K₂SO₄ → BaSO₄ + KNO₃, which implies that KNO₃ will disappear slower from the catalytic surface, thus maintaining the activity for a longer time. It has to be emphasized, that the catalyst prepared using cobalt nitrate, and prepared by sequential impregnation, is the only one that has barium nitrate after calcination. This shows the importance of the selection of the precursor and preparation strategy, in the catalyst design in order to improve its stability in a SO₂ containing atmosphere.

Finally, it is interesting to note that, in the diesel exhaust operation conditions studied in this work, Ba,K,Co_N/CeO₂ (SI) is a good catalyst to abate the soot particles. In an atmosphere containing

real concentrations of NO + O₂ + CO₂ + H₂O at 320 °C, Ba(NO₃)₂ is not carbonated and its presence on the catalytic surface will extend the catalyst lifetime as regard sulfur deactivation. On the other hand, since KNO₃ is not carbonated, the catalytic activity for soot oxidation is preserved. These results show that the Ba,K,Co_N/CeO₂ (SI) is a very suitable catalyst for this reacting system.

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